SPONTANEOUS GENERATION OF HEAT IN RECENTLY HARDENED STEEL.

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(*Read April 22, 1915.*)

Two or three years ago, when studying the behavior, under certain conditions, of several specimens of hardened tool steel, I observed that they all spontaneously generated a small quantity of heat, the amount of which diminished from day to day, but which was observable for several weeks. In each case the steel had been hardened only a few days prior to its use. It seemed highly probable that the generation of heat was associated with some sort of "seasoning" or incipient annealing process, perhaps accompanied by slight change of volume, and that it would be most rapid immediately after hardening. I resolved to investigate this curious phenomenon more fully, but failed to spare the time until a few months ago. This investigation forms the subject of the present paper.

Fig. 1 is a diagram of the apparatus employed. *A, B* represent two large silvered Dewar vacuum jars selected to have very nearly equal thermal insulating efficiency. They are supported in a wooden rack inside a thick copper cylinder *C* packed in granulated cork in a wooden box *E*. *D* is a paper extension of *C*, packed with layers of felt by removal of which and the loose copper cover of *C* easy access is had to the Dewar jars. The copper cylinder weighs 52 pounds and its functions are, by reason of its large thermal capacity and high conductivity, to protect the Dewar jars from any rapid change of temperature, and from temperature stratification.

The box *E* is surrounded by a much larger wooden box *F* lagged with a half-inch layer of felt. A long resistance wire is strung back and forth in the air space between the boxes at the bottom and four sides of *E*. Electric current controlled by a thermostat warms the wire, whereby the temperature of the air space may be maintained very nearly constant as many days or weeks as desired. A

thermometer T, easily read to hundredths of a degree, indicates the temperature of the air space.

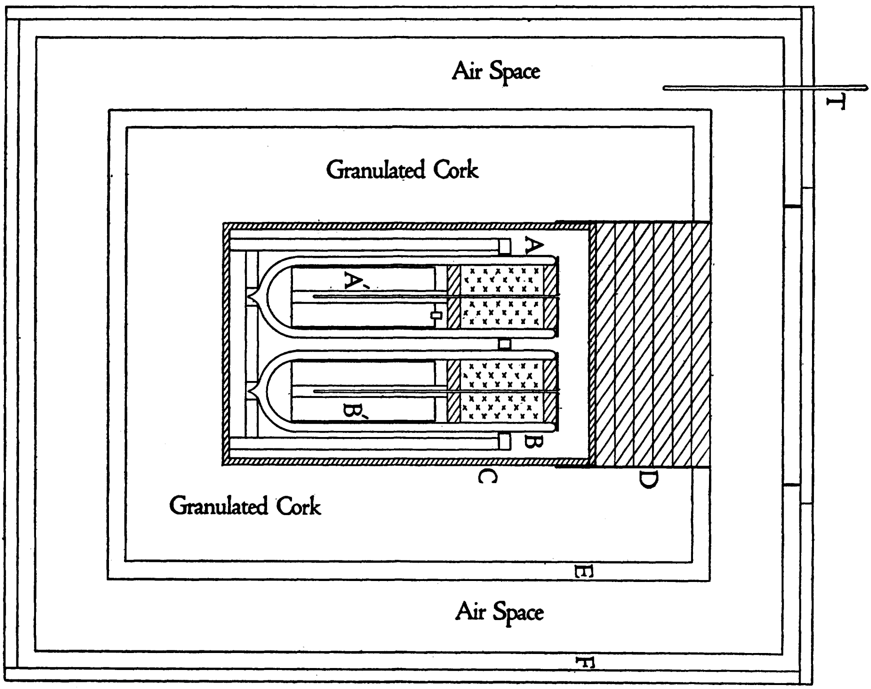

FIG. 1.

Returning now the core of the apparatus: A' is an air-tight cylinder of thin copper, six inches high and two and a half inches in diameter, provided with an open half-inch axial tube also of copper. A small round opening at the top of A' permits the introduction of a weighed quantity of water, after which the opening is tightly corked to prevent any change of temperature by evaporation of the water. B' is another copper cylinder just like A' except that it has a removable top to permit the introduction of the substance whose thermal behavior is to be investigated. The high thermal conductivity of these copper cylinders prevents temperature stratification within them. The Dewar jars are filled above the copper cylinders with layers of felt, and granulated cork, and covered with waxed cardboard carefully sealed on to prevent temperature dif-

ference inside the jars which would follow unequal loss or gain of moisture by the felt and granulated cork. A small thin glass tube, flanged at top and closed at bottom, is located in the axis of each Dewar jar and extends from the waxed cover nearly to the bottom of the inclosed copper cylinder. The glass tubes contain the ends of thermo-electric couples of fine constantan, copper and iron wires, one iron-constantan and one copper-constantan junction at the bottom of each tube. The leading-out wires are copper, and connect the thermo-couples with a reflecting galvanometer having the customary reading telescope and scale. Careful callibration has shown that 55 scale divisions of the galvanometer indicate one degree C. temperature-difference between A' and B', and that temperature-difference and galvanometer deflection are very closely proportional throughout the range used.

In the following experiment A' and B' were removed from the Dewar jars and allowed to attain equal room temperature. Twelve half-inch round bars of tool steel, five inches long and with machined surfaces, were hardened by heating to high "cherry-red" in a reducing atmosphere of a gas furnace and quenching in *cold* water. The bars then had a thin and strongly adhering coating of black oxide. They were next stirred in a large quantity of water at room temperature, to acquire that temperature, wiped dry, and oiled with heavy, neutral mineral oil to prevent generation of heat by further surface oxidation, wiped free of excess of oil and placed in the copper cylinder B'. A weighed quantity of water, also at room temperature, just sufficient to equal the steel bars in thermal capacity had already been placed in A'. The whole apparatus was then assembled as quickly as possible, and galvanometer readings commenced within forty-five minutes of the time of hardening the steel.

The upper curve in Fig. 2 shows the progress of heat generation in the steel bars during the first 150 hours after hardening. A very slow generation of heat was still easily observable at the end of a month.

It is seen that the temperature of the steel bars was rising rapidly when the galvanometer readings commenced, and reached a point (nearly 3° C. at the summit of the curve) where gain and loss of heat balanced each other in about 8 hours.

The "Normal Cooling" curve was obtained five or six weeks after the other, and when the generation of heat had very nearly

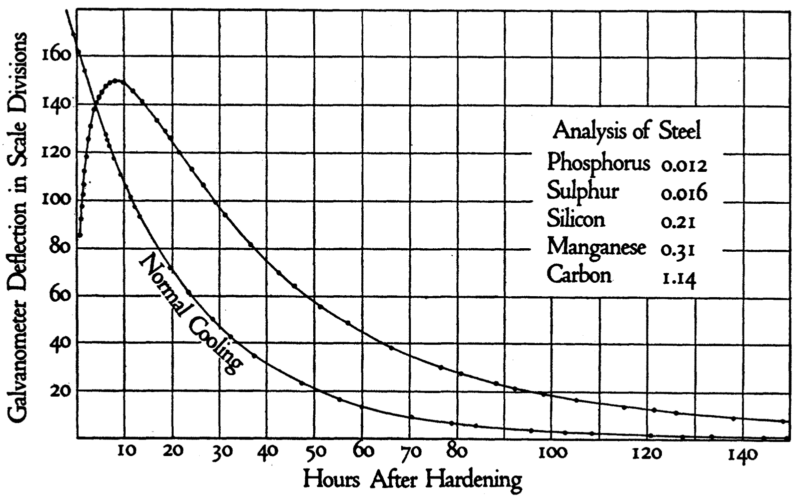

FIG. 2.

ceased. For this purpose the steel bars were removed, warmed a few degrees, and replaced; then galvanometer readings were made from time to time as before. This curve is plotted in a location convenient for visual comparison with the heating curve, but otherwise might just as well be plotted further to the right.

From the two observed curves I have computed a third curve (not shown) which represents the progressive rise in temperature which would have occurred if the thermal insulation of the steel had been perfect, so as to prevent any loss of heat. The curve is strikingly similar in character to the shrinkage curve shown in Fig. 5, and indicates a close association of heat generation and shrinking, to which I shall refer again. The total rise in temperature indicated (about five degrees C.) is of little quantitative importance because it is highly probable that it would have been different if the steel had been hardened at a different temperature, or more uniformly hardened throughout each bar, or had a different carbon content. Yet it is interesting to note that the observed quantity of heat spontaneously generated in the steel, measured by its rise in temperature multiplied by its thermal capacity, indicates internal

work of some sort sufficient to lift the steel bodily about 800 feet high against the force of gravity.

I next prepared a batch of "high-speed" tungsten steel consisting of the same number of bars of the same dimensions as in the first experiment. The bars were water-hardened at white heat, not far below the fusing point, brought to room temperature, oiled and introduced just as in the former case, and galvanometer readings were commenced an hour after hardening.

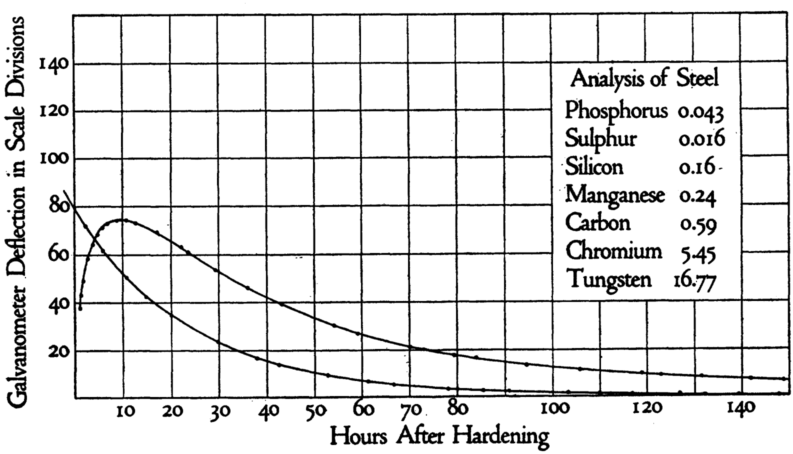

FIG. 3.

Fig. 3 shows the curve of heat generation in the "high-speed" steel, and the curve of normal cooling located with respect thereto as in Fig. 2. The cooling curve here shown is the lower part of that used in Fig. 2. It is permissible to use the same cooling curve for both kinds of steel because the thermal capacity of the two lots was very nearly the same.

It is seen that heat generation in the tungsten steel was the same in character as in the carbon steel of Fig. 2, though much less in amount and somewhat more persistent.

Many workers in steel are aware that the metal expands a little when hardened, and shrinks when annealed; but I have not met with any quantitative data on the subject. With the hope of throwing some light on the spontaneous generation of heat already described, I investigated this phenomenon of swelling and shrinking as follows:

Having no more of the carbon steel used in the first experiment, I procured another half-inch round bar of the same brand, though slightly different in composition as the analyses show. With a piece of this bar two and a half inches long I made a careful determination of its specific gravity under the conditions, and with the results, shown in the following table.

TABLE I.

Specific Gravity		Analysis of Steel	
Commercial Condition	7.8507	Phosphorus	0.015
After Hardening	7.8127	Sulphur	0.021
After Tempering to Light Blue	7.8350	Silicon	0.16
After Annealing	7.8529	Manganese	0.33
		Carbon	1.07

The difference in density and volume between the hardened and annealed conditions is fully a half per cent., which is much more than I expected to find; and nearly half of the total shrinkage was brought about by the very moderate heating necessary for "tempering to light blue." The annealing was very thorough, and, as the figures show, was more complete than in the annealed "commercial condition."

The shrinkage incident to tempering was large enought to encourage the hope that if any spontaneous shrinking, at room temperature, occurs during the generation of heat which follows hardening, it might be detected and measured. For this purpose the apparatus shown in Fig. 4 was designed and constructed.

In Fig. 4 G and H are two vertical steel rods three feet long and one millimeter in diameter. They are hung from a common rigid metal support I, and at their lower ends carry parallel brass bars G', H' which move with perfect freedom, yet in close contact, between guides K, K. The brass bars are accurately machined, and their front edges are polished. The rod G, whose function is purely comparative, is kept under moderate and constant tension by the long spiral spring L; while the rod H carries a four pound weight M. An enlarged sectional diagram at the right shows the method employed in mounting each steel rod. Each end of the rod passes through, and is soldered into, a brass head having a hemi-

spherical end which accurately seats itself in a hollow metal cone. The rods are quickly removable through vertical slots in the cones.

After some preliminary experiments, to get acquainted with the apparatus, a fresh rod *H* was hardened by placing it horizontally in a wooden rack just above a trough of water at room temperature, quickly heating it to bright redness by passing suitable electric

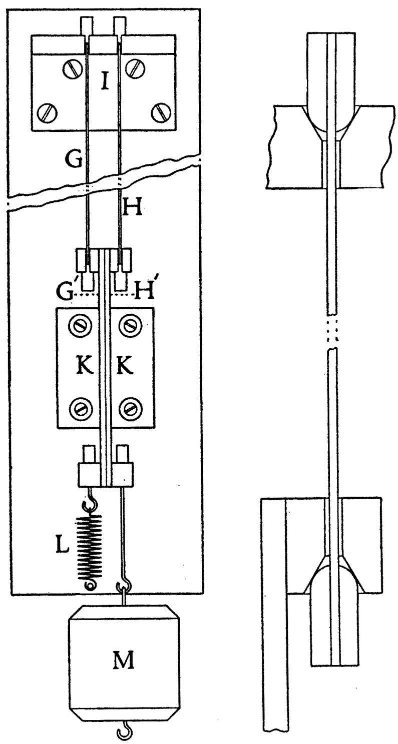

FIG. 4.

current through it and plunging it in the water beneath, the act of lowering the rod serving to break the electric circuit. The rod was kept straight while hot by means of a weak spiral spring which took up the expansion. Preliminary experiments had shown that a rod could be hardened in this way without warping.

The hardened rod, already at room temperature, was quickly wiped dry and put in place beside *G*. Then, without delay, a fine

horizontal scratch was drawn across the polished fronts of the bars G', H' by means of a straight-edge and sharp needle point lightly applied. A microscope, magnifying about 200 diameters and very solidly mounted, was brought into position and focused on the horizontal scratch, which of course consisted of an independent scratch on each bar, the two halves being initially in perfect register. The microscope was provided with a filar micrometer eyepiece carefully calibrated and adapted to measure accurately any departure from register of the two half lines or scratches.

Shrinkage of the hardened rod H was detected within two minutes after scratching the brass bars, and was easily observable at the end of two weeks.

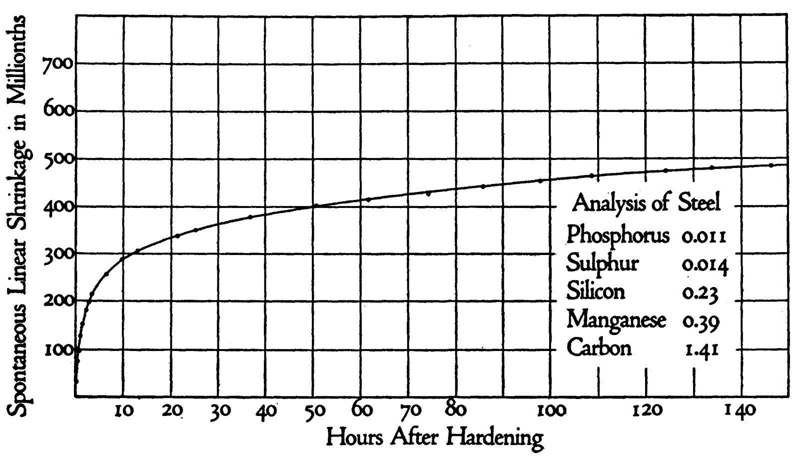

FIG. 5.

Fig. 5 shows the progress of shrinking during the first 150 hours. The curve reached the 500 line a day or two later. The hardened length of the rod was assumed to be 35 inches, so that its actual shrinkage at the 500 line of the curve was 0.0175 inch.

The rod was next scoured clean and tempered to light straw color by electric warming, then to light blue color, and its total shrinkage measured after each operation. Finally, it was thoroughly annealed by bedding in mineral wool, heating to very low redness half an hour, and then gradually reducing the heating current to nothing in the course of two or three hours, after which

the shrinkage was again measured. The rod shrank very considerably in each operation, as indicated quantitatively in Table 2, in which the annealed length is taken as unity or 100 per cent.

TABLE 2.

Length of rod after hardening	100.383
After spontaneous shrinking	100.332
After tempering to light straw	100.182
After tempering to light blue	100.131
After annealing	100.000

Of course the shrinkage in volume must have been very nearly three times the linear shrinkage, or considerably more than one per cent. from the hardened to the annealed condition, which is more than double that observed in the bar steel used in the first experiment. Doubtless this was due to the higher carbon content of the small rod, and more uniform hardening owing to its small size. It is highly probable also that more heat was generated per unit of mass.

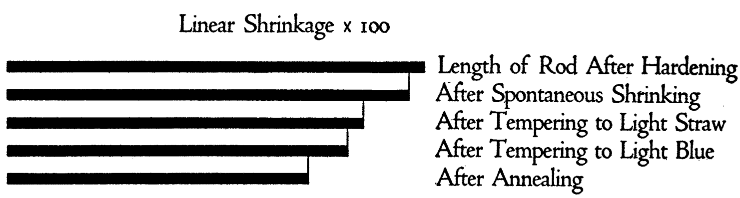

FIG. 6.

In Fig. 6 I have visualized the stages of shrinking of the small rod by magnifying a hundred-fold the observed quantities in Table 2.

I have already pointed out the close similarity in character of the spontaneous-shrinkage curve (Fig. 5) and the computed curve of total heat generation; and there seems little room for doubt that the two phenomena are quantitatively related. But it is equally clear that spontaneous shrinking is only incident to, and is not the prime cause of the generation of heat, because the internal work represented by the heat generated is hundreds of times more than necessary to bring about the accompanying change in volume. This

is found as follows: The small steel rod spontaneously shrank 0.0175 inch. To spring it back to its original length required a weight of 15 pounds hung below *M,* Fig. 4 (= 12.400 pounds strain per square inch of cross-section). Hence, in longitudinally shrinking 0.0175 inch, the rod had done work equal to lifting 15 pounds half this distance or 0.00875 inch. The rod weighed about 1230 times less than the weight, so that the work done was sufficient to lift the rod itself $1230 \times .00875 = 10.76$ inches. But this represents one-dimensional shrinking only, and we must take three times this amount of lift, or, say 2⅔ feet, to represent the work done in the three-dimensional shrinking which certainly occurred. We have already seen that the internal work spontaneously done in the steel bars of the first experiment, in generating the observed amount of heat, was sufficient to lift the bars about 800 feet, which is 300 times greater than the work done in spontaneously shrinking the small rod. If spontaneous shrinkage was less in the large bars than in the small rod, which is highly probable, then this ratio was accordingly greater than three hundred to one. The disparity in weight between the twelve large bars and the one small rod does not count, because the work done in each case is computed for the weight of steel which did it.

It has been suggested that loss of the generated heat may perhaps be regarded as a cooling process without change of temperature (which implies reduction in specific heat), and that this may be sufficient to account for the spontaneous shrinkage. But this hypothesis accounts for only a modest fraction of the shrinkage; while the implied change in specific heat is much too large to be admissible.

An attempt was made to measure Young's modulus of elasticity in the small rod both in the hardened condition (after spontaneous shrinking) and after annealing, by hanging various weights below *M,* Fig. 4, and measuring with the microscope the distortions produced,—always far within the elastic limit. But I was unable to obtain reliable results because of an interesting fact which was brought to light, as follows: In the annealed condition the steel exhibited a small amount of viscosity or internal friction which somewhat delayed full distortion and subsequent restitution; but in the

hardened condition the viscosity was *many times greater*. This is a further illustration of the instability of the hardened steel.

In conclusion, I am led to regard the hardened steel as being in a condition of very great molecular strain somewhat unstable, especially at first. Spontaneous relief of a small portion of the strain causes generation of heat until stability at room temperature is reached. Any considerable rise of temperature, as in tempering, permits further spontaneous relief of strain, or molecular rearrangement, doubtless accompanied by more generation of heat, and so on until annealing temperature is reached. It is obvious that the process of tempering or annealing steel is an exothermic one, and conversely that hardening is an endothermic process.

CLEVELAND,
April, 1915.